

Olivine-type $\text{NaCd}(\text{AsO}_4)$

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Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{As}=\text{O}) = 0.002$ Å; R factor = 0.017; wR factor = 0.043; data-to-parameter ratio = 16.4.

The title compound, sodium cadmium orthoarsenate, adopts the olivine $[\text{Mg}_2(\text{SiO}_4)]$ structure type in space group $Pnma$, with Na (site symmetry $\bar{1}$) and Cd ($.m.$) replacing the two Mg positions, and the AsO_4 tetrahedron ($.m.$) the SiO_4 tetrahedron. The crystal structure is made up of a nearly hexagonal closed-packed arrangement of O atoms stacked along [001]. The Na and Cd atoms occupy one half of the octahedral voids in alternate layers stacked along [100], and one eighth of the tetrahedral voids are occupied by As atoms.

Related literature

For a review of the crystal chemistry of olivines, see: Brown (1982). For the isotopic phosphate analogue, see: Ivanov *et al.* (1974); Hata *et al.* (1979). For other phases in the system $\text{Na}–\text{Cd}–\text{P}–\text{O}$, see: Murashova & Chudinova (1997); Bennazha *et al.* (2000); Ben Amara *et al.* (1979). For standardization of structure data, see: Gelato & Parthé (1987).

Experimental

Crystal data

$\text{NaCd}(\text{AsO}_4)$	$V = 382.47$ (10) Å ³
$M_r = 274.32$	$Z = 4$
Orthorhombic, $Pnma$	Mo $K\alpha$ radiation
$a = 11.1585$ (17) Å	$\mu = 14.27$ mm ⁻¹
$b = 6.550$ (1) Å	$T = 293$ K
$c = 5.2330$ (8) Å	$0.06 \times 0.04 \times 0.04$ mm

Data collection

Bruker SMART CCD diffractometer	4252 measured reflections
Absorption correction: multi-scan (<i>SADABS</i> ; Bruker, 2005)	656 independent reflections
$(SADABS$; Bruker, 2005)	615 reflections with $I > 2\sigma(I)$
$T_{\min} = 0.481$, $T_{\max} = 0.599$	$R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.017$	40 parameters
$wR(F^2) = 0.043$	$\Delta\rho_{\text{max}} = 0.67$ e Å ⁻³
$S = 1.10$	$\Delta\rho_{\text{min}} = -0.75$ e Å ⁻³
656 reflections	

Table 1
Selected bond lengths (Å).

Cd–O2	2.229 (3)	Na–O3 ^v	2.3814 (18)
Cd–O1 ⁱ	2.2629 (18)	Na–O3 ^{vi}	2.3814 (18)
Cd–O1 ⁱⁱ	2.2629 (18)	Na–O1 ^v	2.5031 (18)
Cd–O3	2.321 (2)	Na–O1 ^{vi}	2.5031 (18)
Cd–O1	2.4030 (18)	As–O3 ^{vii}	1.677 (2)
Cd–O1 ⁱⁱⁱ	2.4030 (18)	As–O2 ^{viii}	1.687 (2)
Na–O2	2.3779 (19)	As–O1 ⁱⁱⁱ	1.7030 (17)
Na–O2 ^{iv}	2.3779 (19)	As–O1	1.7030 (17)

Symmetry codes: (i) $-x + \frac{1}{2}, y + \frac{1}{2}, z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, -y, z + \frac{1}{2}$; (iii) $x, -y + \frac{1}{2}, z$; (iv) $-x, -y, -z$; (v) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (vi) $-x + \frac{1}{2}, -y, z - \frac{1}{2}$; (vii) $x, y, z - \frac{1}{2}$; (viii) $x + \frac{1}{2}, y, -z + \frac{1}{2}$.

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS for Windows* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: PJ2006).

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supplementary materials

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1. Comment

Up to now there are no reports on crystal structure determinations of phases in the system $\text{Na}-\text{Cd}-\text{As}-\text{O}$, whereas for the analogous system $\text{Na}-\text{Cd}-\text{P}-\text{O}$ several phases with compositions $\text{NaCd}(\text{PO}_4)$ (Ivanov *et al.*, 1974; Hata *et al.*, 1979), $\text{NaCd}(\text{PO}_3)_3$ (Murashova & Chudinova, 1997), $\text{Na}_2\text{Cd}_3(\text{P}_2\text{O}_7)_2$ (Bennazha *et al.*, 2000) and $\text{Cd}_4\text{Na}(\text{PO}_4)_3$ (Ben Amara *et al.*, 1979) have been structurally fully characterized. In this article the synthesis and crystal structure of $\text{NaCd}(\text{AsO}_4)$ is reported.

$\text{NaCd}(\text{AsO}_4)$ crystallizes in the olivine $[\text{Mg}_2(\text{SiO}_4)]$ structure type. A review on the crystal chemistry of olivines and spinels has been published some time ago by Brown (1982). The olivine structure is characterized by an almost hexagonal closed-packed arrangement of oxygen atoms parallel to (001) with a stacking sequence *ABAB* along [001] with one half of the octahedral voids occupied by magnesium sites, and one-eighth of the tetrahedral voids by silicon sites. In the structure of $\text{NaCd}(\text{AsO}_4)$, the two magnesium sites and the silicon site are replaced by unique sodium and cadmium sites and an arsenic site, respectively. The resulting NaO_6 octahedron has $\bar{1}$ symmetry, and the CdO_6 octahedron and the AsO_4 tetrahedron both have *m*. symmetry.

In comparison with the isotypic structure of $\text{NaCd}(\text{PO}_4)$ (Ivanov *et al.*, 1974), the $\text{Cd}-\text{O}$ and $\text{Na}-\text{O}$ distances are virtually the same, with mean bond lengths for the CdO_6 and NaO_6 octahedra of 2.307 (71) Å and 2.398 (54) Å in the phosphorus compound, and of 2.314 (75) Å and 2.421 (64) Å, respectively, in the arsenic compound. As expected, only the distances within the PO_4 (mean $\text{P}-\text{O}$ distance 1.541 (12) Å) and AsO_4 (1.693 (13) Å) tetrahedra differ, because of the different sizes of $\text{P}(\text{V})$ and $\text{As}(\text{V})$.

2. Experimental

To an aqueous 0.05 *M* solution (20 ml) of cadmium acetate, an aqueous solution of 0.05 *M* Na_2HAsO_4 (20 ml) was added. Together with the mother liquor, parts of the colourless precipitate were transferred to a 10 ml Teflon insert (filling degree one-half). The insert was then sealed and heated in a steel autoclave under autogenous pressure at 338 K for ten days. Few colourless single crystals of the title compound with a block-like form were obtained after the reaction time, and were manually separated from the reaction mixture that was not further examined.

3. Refinement

Atomic coordinates of the isotypic $\text{NaCd}(\text{PO}_4)$ (Ivanov *et al.*, 1974) in space group *Pnma* were taken as starting parameters for refinement of $\text{NaCd}(\text{AsO}_4)$. Besides a structure refinement of $\text{NaCd}(\text{PO}_4)$ in *Pnma*, also refinements of this structure in the non-centrosymmetric space group No. 33 were performed with settings in *Pn2₁a* (Ivanov *et al.*, 1974) and *P2₁nb* (Hata *et al.*, 1979). However, adopting these non-centrosymmetric structure models for refinement of $\text{NaCd}(\text{AsO}_4)$ converged with significantly higher residual parameters and with large correlation matrix elements. Therefore the structure model in space group *Pnma* was considered as being correct, in agreement with other olivine-type structures.

Structure data were finally standardized with *STRUCTURE TIDY* (Gelato & Parthé, 1987).

Computing details

Data collection: *SMART* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* (Bruker, 2005); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS for Windows* (Dowty, 2006); software used to prepare material for publication: *publCIF* (Westrip, 2010).

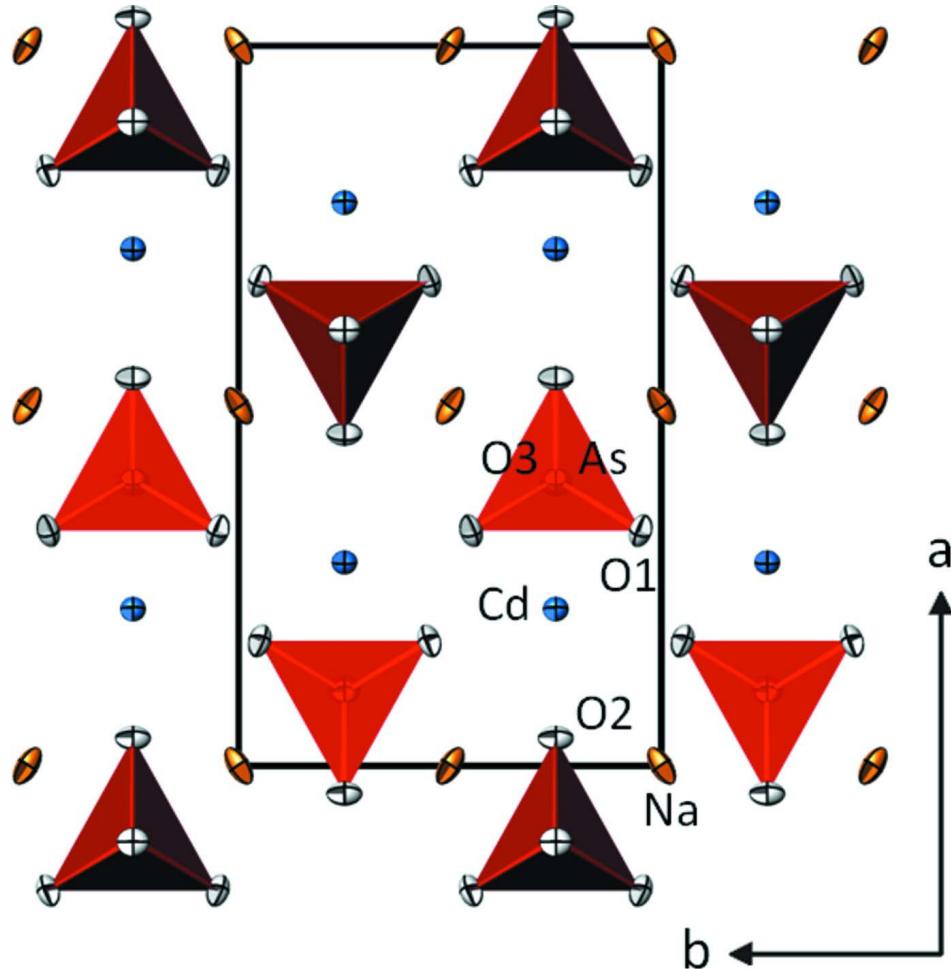


Figure 1

The olivine-type crystal structure of $\text{NaCd}(\text{AsO}_4)$ in a projection along [001]. Displacement ellipsoids are drawn at the 74% probability level.

Sodium cadmium orthoarsenate

Crystal data

$\text{NaCd}(\text{AsO}_4)$
 $M_r = 274.32$
Orthorhombic, $Pnma$
Hall symbol: -P 2ac 2n
 $a = 11.1585 (17) \text{ \AA}$
 $b = 6.550 (1) \text{ \AA}$
 $c = 5.2330 (8) \text{ \AA}$

$V = 382.47 (10) \text{ \AA}^3$
 $Z = 4$
 $F(000) = 496$
 $D_x = 4.764 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Cell parameters from 2012 reflections
 $\theta = 3.7\text{--}30.9^\circ$

$\mu = 14.27 \text{ mm}^{-1}$
 $T = 293 \text{ K}$

Block, colourless
 $0.06 \times 0.04 \times 0.04 \text{ mm}$

Data collection

Bruker SMART CCD diffractometer
 Radiation source: fine-focus sealed tube
 Graphite monochromator
 ω scans
 Absorption correction: multi-scan (SADABS; Bruker, 2005)
 $T_{\min} = 0.481$, $T_{\max} = 0.599$

4252 measured reflections
 656 independent reflections
 615 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$
 $\theta_{\max} = 31.0^\circ$, $\theta_{\min} = 3.7^\circ$
 $h = -16 \rightarrow 15$
 $k = -8 \rightarrow 9$
 $l = -7 \rightarrow 7$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.017$
 $wR(F^2) = 0.043$
 $S = 1.10$
 656 reflections
 40 parameters
 0 restraints

Primary atom site location: structure-invariant direct methods
 Secondary atom site location: difference Fourier map
 $w = 1/[\sigma^2(F_o^2) + (0.0225P)^2 + 0.1997P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.67 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.75 \text{ e \AA}^{-3}$

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cd	0.21753 (2)	0.2500	0.50818 (5)	0.00974 (8)
Na	0.0000	0.0000	0.0000	0.0140 (3)
As	0.39805 (3)	0.2500	0.06207 (6)	0.00795 (9)
O1	0.32677 (15)	0.0493 (3)	0.2024 (3)	0.0122 (3)
O2	0.0386 (2)	0.2500	0.3191 (5)	0.0127 (5)
O3	0.3944 (2)	0.2500	0.7417 (5)	0.0116 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cd	0.00894 (13)	0.00954 (14)	0.01073 (13)	0.000	0.00028 (7)	0.000
Na	0.0209 (7)	0.0128 (8)	0.0084 (7)	0.0086 (6)	-0.0005 (5)	-0.0027 (5)
As	0.00785 (16)	0.00855 (18)	0.00743 (16)	0.000	0.00039 (11)	0.000
O1	0.0157 (8)	0.0086 (8)	0.0124 (8)	-0.0029 (6)	0.0025 (6)	0.0004 (6)
O2	0.0088 (10)	0.0188 (14)	0.0106 (11)	0.000	0.0015 (8)	0.000
O3	0.0119 (11)	0.0158 (13)	0.0069 (10)	0.000	0.0003 (8)	0.000

Geometric parameters (\AA , $\text{\textit{\AA}}$)

Cd—O2	2.229 (3)	Na—O3 ^v	2.3814 (18)
Cd—O1 ⁱ	2.2629 (18)	Na—O3 ^{vi}	2.3814 (18)
Cd—O1 ⁱⁱ	2.2629 (18)	Na—O1 ^v	2.5031 (18)
Cd—O3	2.321 (2)	Na—O1 ^{vi}	2.5031 (18)
Cd—O1	2.4030 (18)	As—O3 ^{vii}	1.677 (2)
Cd—O1 ⁱⁱⁱ	2.4030 (18)	As—O2 ^{viii}	1.687 (2)
Na—O2	2.3779 (19)	As—O1 ⁱⁱⁱ	1.7030 (17)
Na—O2 ^{iv}	2.3779 (19)	As—O1	1.7030 (17)
O2—Cd—O1 ⁱ	90.21 (5)	O3 ^v —Na—O1 ^{vi}	98.07 (7)
O2—Cd—O1 ⁱⁱ	90.21 (5)	O3 ^{vi} —Na—O1 ^{vi}	81.93 (7)
O1 ⁱ —Cd—O1 ⁱⁱ	120.07 (9)	O1 ^v —Na—O1 ^{vi}	180.00 (5)
O2—Cd—O3	174.59 (9)	O3 ^{vii} —As—O2 ^{viii}	113.04 (12)
O1 ⁱ —Cd—O3	87.09 (5)	O3 ^{vii} —As—O1 ⁱⁱⁱ	114.82 (8)
O1 ⁱⁱ —Cd—O3	87.09 (5)	O2 ^{viii} —As—O1 ⁱⁱⁱ	105.97 (8)
O2—Cd—O1	99.14 (7)	O3 ^{vii} —As—O1	114.82 (8)
O1 ⁱ —Cd—O1	152.11 (7)	O2 ^{viii} —As—O1	105.97 (8)
O1 ⁱⁱ —Cd—O1	86.33 (4)	O1 ⁱⁱⁱ —As—O1	101.06 (12)
O3—Cd—O1	85.37 (7)	As—O1—Cd ^{vi}	125.24 (9)
O2—Cd—O1 ⁱⁱⁱ	99.14 (7)	As—O1—Cd	95.84 (8)
O1 ⁱ —Cd—O1 ⁱⁱⁱ	86.33 (4)	Cd ^{vi} —O1—Cd	131.47 (7)
O1 ⁱⁱ —Cd—O1 ⁱⁱⁱ	152.11 (7)	As—O1—Na ⁱⁱ	90.41 (7)
O3—Cd—O1 ⁱⁱⁱ	85.37 (7)	Cd ^{vi} —O1—Na ⁱⁱ	109.66 (7)
O1—Cd—O1 ⁱⁱⁱ	66.33 (8)	Cd—O1—Na ⁱⁱ	92.76 (6)
O2—Na—O2 ^{iv}	180.00 (9)	As ^v —O2—Cd	132.00 (14)
O2—Na—O3 ^v	89.37 (6)	As ^v —O2—Na	95.20 (9)
O2 ^{iv} —Na—O3 ^v	90.63 (6)	Cd—O2—Na	118.29 (8)
O2—Na—O3 ^{vi}	90.63 (6)	As ^v —O2—Na ^{ix}	95.20 (9)
O2 ^{iv} —Na—O3 ^{vi}	89.37 (6)	Cd—O2—Na ^{ix}	118.29 (8)
O3 ^v —Na—O3 ^{vi}	180.00 (10)	Na—O2—Na ^{ix}	87.04 (9)
O2—Na—O1 ^v	67.30 (7)	As ^x —O3—Cd	123.17 (13)
O2 ^{iv} —Na—O1 ^v	112.70 (7)	As ^x —O3—Na ⁱⁱ	121.26 (9)
O3 ^v —Na—O1 ^v	81.93 (7)	Cd—O3—Na ⁱⁱ	98.11 (8)
O3 ^{vi} —Na—O1 ^v	98.07 (7)	As ^x —O3—Na ^{xi}	121.26 (9)
O2—Na—O1 ^{vi}	112.70 (7)	Cd—O3—Na ^{xi}	98.11 (8)
O2 ^{iv} —Na—O1 ^{vi}	67.30 (7)	Na ⁱⁱ —O3—Na ^{xi}	86.89 (8)

Symmetry codes: (i) $-x+1/2, y+1/2, z+1/2$; (ii) $-x+1/2, -y, z+1/2$; (iii) $x, -y+1/2, z$; (iv) $-x, -y, -z$; (v) $x-1/2, y, -z+1/2$; (vi) $-x+1/2, -y, z-1/2$; (vii) $x, y, z-1$; (viii) $x+1/2, y, -z+1/2$; (ix) $-x, y+1/2, -z$; (x) $x, y, z+1$; (xi) $x+1/2, -y+1/2, -z+1/2$.